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Rubber Seed Shell Biochar Sulphonation: A Process Optimization and Conditions' Effect Analysis

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Abstract

This study investigated the sulphonation process of biochar prepared from the carbonization of rubber seed shells. The biochar was sulphonated using 98% concentrated sulphuric acid, and the total acid density on the surface of the sulphonated biochar was determined using acid-base back titration. The effect of sulphonation process variables including acid-to-biochar ratio, sulphonation time, and sulphonation temperature on the biochar's total acid density was studied. The process was optimized using response surface methodology with a central composite design. The results revealed that a quadratic polynomial model best described the sulphonation process of rubber seed shell biochar with no significant lack of fit. An optimum total acid density of 3.08 mmol/g was obtained under an acid-to-biochar ratio of 10:1 (v/w), sulphonation time of 4.00 hr., and sulphonation temperature of 98.08 ºC. The large total acid density of the rubber seed shells biochar makes it a potential esterification catalyst for biodiesel production.

1. Introduction

The similarities in the physico-chemical properties of biodiesel and petro-diesel, and the fact that biodiesel is renewable, environment-friendly, and not toxic make biodiesel an alternative source of diesel fuel [1]. Transesterification is a widely used method of biodiesel production that involves the reaction of vegetable oil or animal fat with alcohol in the presence of a catalyst [2, 3]. Homogeneous and heterogeneous catalysts have been used in the transesterification of vegetable oil. Due to the drawbacks of homogeneous catalyst (such as non-reusability, soap formation in the case of homogeneous base catalyst, corrosion of process equipment in the case of homogeneous base catalyst, and difficulty in product separation), interest in the use of the heterogeneous catalyst for biodiesel production has increased in recent time. The use of biomass such as shells, bones, brewery wastes, and carbon-based biomass to synthesize heterogeneous catalysts has gained a whole heap of attention because they are renewable and sustainable with zero-emission [4, 5, 6].

For effective catalytic activity, carbon-based catalysts for biodiesel synthesis through esterification must have high acid site density and good pore size. Carbon can be categorized as either amorphous or crystalline carbon. Amorphous carbons, such as the conventional activated carbons and biochars, have been discovered to have a more promising surface structure because of their high micropore and mesopore volumes and the associated high surface area, which increases the sites for active group attachments [7]. Porous carbon from biomass can be synthesized in three ways: pyrolysis, gasification, hydrothermal carbonization, and torrefaction [8]. Pyrolysis and gasification require greater temperatures in the ranges of 300 to 600 ^oC and 300 to 900 ^oC respectively, whereas hydrothermal carbonization and torrefaction require lower temperatures of 200 to 300 ^oC [9]. The most extensively utilized carbonization process for the manufacture of biochar is pyrolysis. In the process of pyrolysis, the various constituents of the biomass (lignin, cellulose, and hemicellulose) undergo several thermochemical reaction pathways which include depolymerization, fragmentation, and cross-linkage, to generate solid, liquid, and gaseous products known as biochar, bio-oil, and biogas respectively [10, 11, 12]. The surface properties of the biochar are influenced by many factors such as pyrolysis temperature and time. Lou et al. [13] reported that increasing the pyrolysis temperature of starch increased the surface properties of the resulting biochar and consequently, the overall increase in the activity of the catalyst synthesized from the biochar.

Typically, the acid density of biochars is very low due to the presence of a few functional groups (–OH and -COOH) on the polycyclic aromatic carbon sheet. Consequently, raw biochar cannot be used as a catalyst in the production of biodiesel. It must possess a very high acid density, which can only be achieved through a process known as sulphonation. Sulphonation is the attachment of acid functional groups such as the sulphonic ($-SO_3H$) group to the surface of the carbon to enhance its total acid density using (95%-98%) concentrated sulphuric acid [14], fuming sulphuric acid [15], 4-Benzenediazoniumsulphonate [16], or p-toluene sulphonic acid [17]. It has been reported that the attachment of the sulphonic group on the surface of the biochar is influenced by several factors including the nature of the starting biomass, sulphonation temperature, and time [7]. Although several kinds of research related to the sulphonation of biochar have been conducted, an effort has not been made to optimize the process to determine the best selection of process variables for maximum attachment of the sulphonic group to the surface of the biochar. This study, therefore, was aimed at conducting a sulphonation process optimization and investigating the effect of process variables on the total acid density of the biochar produced from rubber seed shells (RSS) using response surface methodology.

2. Methodology

2.1 Materials and Methods

Rubber seeds were sourced from the Rubber Research Institute of Nigeria (RRIN), Iyanomo, Edo State, Nigeria. The seeds were crushed with mortar and pestle to aid the separation of the kernel from the shell. The separated shells were washed with clean water to remove any adhering contaminants. The washed shells were dried in the oven for 3 hrs at 105^oC and stored in an air-tight jar after cooling to room temperature in a desiccator. The reagents (hydrochloric acid solution, fuming sulphuric acid, phenolphthalein indicator, and potassium hydroxide,) used in this study were of analytical grade.

2.2. Carbonization of the Rubber seed shell

Rubber seed biochar was produced from the carbonization of rubber seed shells using the pyrolysis method as outlined by Naeem et al. [3]. Dried RSS was pulverized with mortar and pestle to reduce its size to an average of about 250 µm. The carbonization of the pulverized RSS was done in a two-step procedure which included chemical pretreatment and pyrolysis.

The chemical pretreatment of the pulverized RSS involved the treatment of 20g of the sample with 98% sulphuric acid solution in a beaker. The content of the beaker was continuously stirred for a period of 1 hr. At every interval of 10 mins, 10 ml of de-ionized water was added to the content of the beaker to lower its viscosity for efficient stirring. After the set duration of agitation, the beaker containing the slurry was covered with a lid to prevent contamination with environmental impurities and the slurry was kept in the laboratory for 24 hrs. After that, the partially carbonized RSS was washed twice with 100 ml of distilled water. The acid left in the partially carbonized RSS was then neutralized with a saturated sodium hydroxide solution, and steadily added to the sample with constant stirring until neutralization was complete as indicated by the pH meter. The neutralized slurry was filtered and the resulting black residue (partially carbonized RSS) was dried at 105 ^oC for 3 hrs in the oven.

The second stage of the carbonization involved the slow pyrolysis of the partially carbonized RSS in a heating furnace (Narbetherm, P300) under N_2 flow at 600 ^oC for 4 hrs. The completely carbonized RSS was allowed to cool in a desiccator. After cooling, the biochar was demineralized by washing with hot distilled water twice to remove any adhering impurities arising from the pyrolysis. The biochar, after demineralization, was dried in the oven at 105 ^oC for 3 hrs.

2.3. Sulphonation of rubber seed shells

The rubber seed shells biochar was sulphonated using concentrated sulphuric acid (98%) to introduce the sulphonic group into the polycyclic aromatic sheet present in the biochar [14]. This was performed by mixing in a 250 ml capacity conical flask, 2g of RSS-BC with an appropriate volume of 98% of sulphuric acid, based on the desired acid/biochar ratio (v/w) as indicated in the design of the experiment (Table 1). The mixture was first stirred for 20 mins; then the residual mixture was heated in a crucible and placed inside a heating furnace at various temperatures and times (see Table 1). After the stipulated Sulphonation time elapsed, the mixture was allowed to cool to room temperature after which it was washed repeatedly with 250 ml of hot distilled water at a temperature of 85 ^oC until a neutral pH of the wash water was obtained. The sulphonated biochar was dried in the oven at a temperature of 105 ^oC for 2 hrs to ensure total moisture removal from the catalyst.

2.4. Determination of total acid density of the sulphonated biochar

Acid-base back titration was employed to determine the total acid density of the sulphonated rubber seed shells biochar by exchanging protons between a standard aqueous solution of sodium hydroxide and the catalyst sample in a process known as back titration. The procedure described by Ezebor et al. [15] was adopted. A catalyst sample weighing 0.02 g was added to a beaker containing 25 ml of a standard solution of sodium hydroxide (0.02 M NaOH). The mixture was vigorously agitated for 45 minutes using a magnetic stirrer and separated with filter paper. The filtrate (excess sodium hydroxide solution) was back-titrated against a standard solution of 0.05 M HCl using phenolphthalein as an indicator. The volume of hydrochloric acid required to neutralize the excess sodium hydroxide solution was then noted. The total acid density of the biochar sample was thereafter calculated from the number of moles of sodium hydroxide consumed.

2.5. Design of experiment

The effects of acid-to-biochar ratio (X_1), Sulphonation temperature (X_2), and Sulphonation time (X_3) on the total acid density (Y) of biochar were investigated using response surface methodology with a central composite design (CCD) of the experiment at five different variable levels. The factors were coded using Eq. 1, and the actual and coded levels of these factors are shown in Table 1. The total acid density on the surface of the resulting catalyst was taken as the process response. The experimental data obtained from the Sulphonation process of the rubber seed shells were analyzed for the response and optimum values of the variables by the polynomial equation (Equation 2).

$$x_i = \frac{X_i - X_o}{\Delta X_i} \quad 1$$

$$\mathrm{Y} = \mathrm{b_o} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{b_i X_i} + \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{b_{ii} X_i^2} + \sum_{\mathrm{i>j}}^{\mathrm{n}} \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{b_{ij} X_i X_j} + \mathrm{e} \quad 2$$

Y is the response representing the total acid density of the sulphonated biochar. X_i and X_j are the independent variables, while b_o, b_i, b_{ii}, and b_{ij} are the intercept, first-order coefficient of the model, quadratic coefficient of the i^{th} variable, and linear coefficient of the model for i^{th} and j^{th} variable interaction respectively. n is the number of factors and e is the error term.

Table 1: Coded and actual values for the Sulphonation process of rubber seed shells biochar

Variables	Symbols	Coded and Actual Levels				
		-2	-1	0	1	2
Acid-to-biochar ratio (v/w)	X_1	2:1	4:1	6:1	8:1	10:1
Sulphonation temperature (°C)	X_2	70	80	90	100	110
Sulphonation time (hr)	X_3	2	4	6	8	10

3. Results and Discussion

3.1. Model development and its analysis for the process

The results of the seventeen experimental runs conducted to study the effect of sulphonation process parameters on the total acid density of the sulphonated rubber seed shells biochar are shown in the experimental design matrix presented in Table 2. The experimentally observed maximum and minimum values of the total acid density on the surface of the sulphonated RSS-BC, within the ranges of values of the process variables studied, were 3.11 mmol/g and 2.69 mmol/g respectively and the average value was 2.87 mmol/g.

Multiple linear regression analyses on the experimental data revealed that a polynomial quadratic model described the relationship between the process variables and the response. The quadratic model in terms of the actual values is shown in Eq. 3.

$$\begin{aligned} Y = -0.42837 - 0.035041X_1 + 0.068372X_2 + 0.054158X_3 + 0.0013125X_1X_2 \\ - 0.000625X_1X_3 + 0.001875X_2X_3 - 0.035326X_1^2 - 0.0004538X_2^2 \\ - 0.02163X_3^2 \end{aligned} \quad 3$$

Y is the total acid density on the sulphonated RSS-BC (mmol/g), X_1 is the acid/biochar ratio (v/w), X_2 is the sulphonation temperature (°C), and X_3 is the sulphonation time (hr).

The significance and goodness of fit of the quadratic model were investigated by performing an analysis of variance (ANOVA). The results of the ANOVA conducted on the data from the sulphonation of rubber seed shells biochar are presented in Table 3. The model's F-value was 24.82. The likelihood that this large F-value of the model has resulted from noise is just 0.02%, indicating that the model is not insignificant. The p-value (Prob > F) of 0.0002 further validated the statistical significance of the model with a confidence interval of 95%, since the model's p-value was less than 0.05. Higher p-values (p-value > 0.1) indicate that the model or its terms were not significant. Consequently, all the model terms except X_1X_3 and X_2X_3 were statistically significant. The insignificant nature of X_1X_3 and X_2X_3 implies that the influence of acid-to-biochar ratio on the total acid density of the biochar is not significantly affected by the duration of sulphonation. Also, the total acid density is affected by changes in sulphonation temperature, regardless of the duration of sulphonation and vice-versa. However, all the terms of the model were retained to enhance its accuracy and minimize the discrepancies between the observed and predicted responses [18]. The model had a lack of fit's F-value of 0.96, which meant that the model's lack of fit was insignificant with respect to the pure error. An insignificant lack of fit is desirable because the model is required to fit the experimental data adequately.

On the other hand, the coefficient of determination (R^2) of the model was found to be 0.9696. The closer the R^2 value to 1, the higher the robustness of the model. An R^2 value of one indicates a sure-fire model. The R^2 value of 0.969 obtained for this model, therefore, implied that the model was able to account for 96.96% of the observed variability in the response of the sulphonation process of rubber seed shell biochar. Comparing the adjusted R^2 (0.9306) and the predicted R^2 (0.805) showed a disparity of only 0.1256, suggesting a robust correlation. This is further validated by the correlation variation (C.V.) value of 1.11%, which is less than 10%, implying an adequate correlation between the predicted and observed response as shown in Fig. 1. The model's signal-to-noise ratio, indicated by its adeq. precision value of 16.063 (adeq.> 4) signified adequate signal. It means, therefore, that the model can adequately and suitably fit into the design space.

Table 2: Experimental design matrix showing the process factors and the corresponding response

Run	Factors			Response
	X_1 -Acid/biochar (v/w)	X_2 -Sulphonation temperature (oC)	X_3 -Sulphonation time (hr)	Total acid density (mmol/g)
1	4	90	3	2.82
2	10	80	4	2.93
3	10	100	4	3.11
4	8	90	3	2.96
5	10	80	2	2.81
6	8	90	3	2.97
7	8	110	3	2.81
8	6	100	2	2.71
9	6	100	4	2.91
10	6	80	2	2.71
11	8	90	5	3.03
12	8	90	1	2.69
13	10	100	2	2.87
14	8	70	3	2.72
15	12	90	3	2.96
16	6	80	4	2.88
17	8	90	3	2.91

Table 3: ANOVA for the quadratic polynomial model of the sulphonation process of rubber seed shells

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-Value**	**p-value Prob > F**	
Model	0.225	9	0.0250	24.8246	0.0002	significant
X_1-Acid/biochar	0.03901	1	0.0390	38.7251	0.0004	
X_2-Sulphonation temp.	0.01266	1	0.0127	12.5650	0.0094	
X_3-Sulphonation time	0.12426	1	0.1243	123.3607	< 0.0001	
X_1X_2	0.00551	1	0.0055	5.4728	0.0519	
X_1X_3	0.00001	1	0.0000	0.0124	0.9144	
X_2X_3	0.00281	1	0.0028	2.7922	0.1386	
X_1^2	0.00387	1	0.0039	3.8394	0.0909	
X_2^2	0.03989	1	0.0399	39.5995	0.0004	
X_3^2	0.00906	1	0.0091	8.9967	0.0200	
Residual	0.007	7	0.001			
Lack of Fit	0.005	5	0.001	0.965	0.5799	Not significant
Pure Error	0.002	2	0.001			
Cor Total	0.232	16		R^2	0.9696	
C.V. %	1.11			Adj R^2	0.9306	
Adeq. Prec.	16.063			Pred. R^2	0.805	

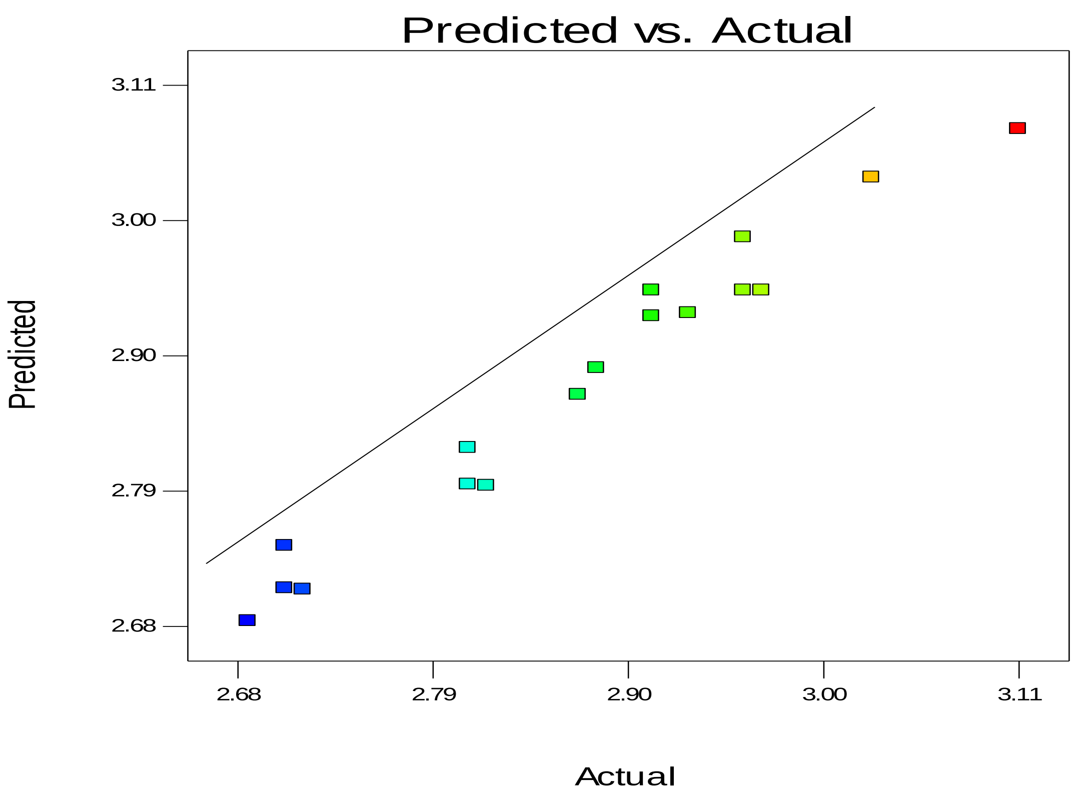

Figure 1: Actual vs predicted values of total acid density of sulphonated rubber seed shells biochar

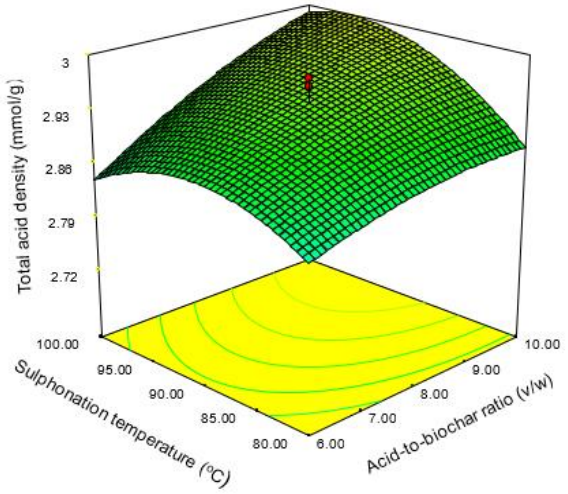

Figure 2(a): Interaction effect of temperature and acid/biochar on total acid density

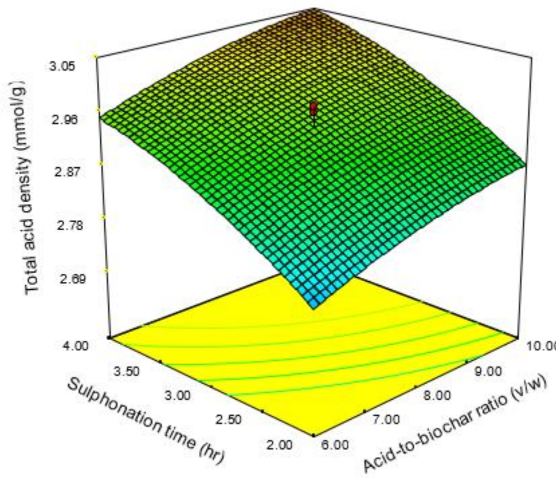

Figure 2(b): Interaction effect of sulphonation time and acid/biochar ratio on total acid density

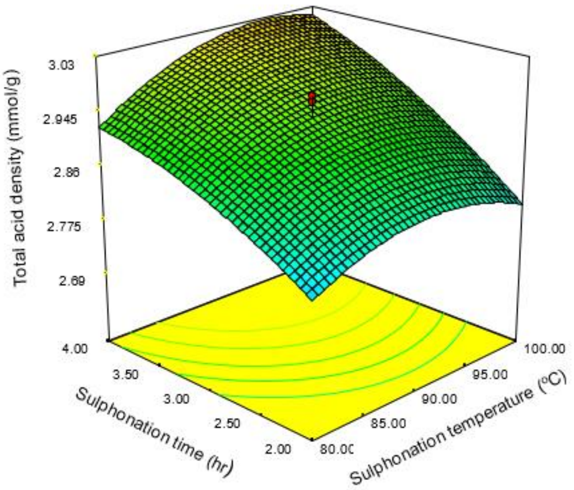

Figure 2(c): Interaction effect of sulphonation time and temperature on total acid density

3.3. Effect of interaction of process factors on the total acid density

The effects of process factors and their interaction on the total acid density of the sulphonated biochar are shown by the response surface profiles presented in Fig. 2. The interaction effect of acid-to-biochar ratio and sulphonation temperature is shown in Fig. 2(a). The response surface profile revealed that the total acid density of the sulphonated biochar increased with an increase in both acid-to-biochar ratio and sulphonation temperature. The effect of sulphonation temperature on the total acid density was more pronounced at a higher acid-to-biochar ratio than at a lower value. Total acid density increased with temperature until it reached a maximum point and began to decrease slightly with a further increase in sulphonation temperature. A similar trend was reported by Endut et al. [19] in the study of "optimization of biodiesel production by solid acid catalyst derived from coconut shell via response surface methodology". They observed that the catalyst produced from the sulphonation of coconut shell biochar at a lower temperature of 100 ^{o}C rather than a higher temperature of 200 ^{o}C, was much more effective and efficient. It, therefore, implies that the attachment of sulphonic group (-SO_3H) unto the polycyclic aromatic sheet of the biochar is enhanced at a lower sulphonation temperature [19, 20].

Fig. 2(b) is the 3-D response surface plot showing the variation of total acid density with sulphonation time and acid-to-biochar ratio. It was observed that increasing sulphonation time and acid-to-biochar ratio concurrently, within the ranges of the variables studied, increased the total acid density of the biochar. Increasing the acid-to-biochar ratio increased the availability of sulphonic groups and their subsequent adsorption on the surface of the biochar, thereby increasing the total acid density of the biochar [21]. Higher acid-to-biomass ratios in the range of 8:1 to 12:1 have been reported in the literature for the sulphonation of biochar prepared from different agricultural biomass [14, 19, 22], and the findings in this study fall within this range.

The variation and interaction effect of sulphonation temperature and sulphonation time on the total acid density of sulphonated RSS-BC is as shown in Fig. 2(c). When the sulphonation temperature was increased from 80 ^oC to 100 ^oC, the total acid density of the biochar increased gradually to a maximum value, and began to decrease when the sulphonation temperature was further increased, regardless of the duration of sulphonation. Similarly, the total acid density of the biochar increased with an increase in the sulphonation time, irrespective of the duration of sulphonation. This finding confirms the insignificance of the interaction between the sulphonation time and sulphonation temperature as stated in the ANOVA. The prolonged sulphonation process enhanced adequate exposure of the sulphonic group to the micropores of the biochar resulting in an increased total acid density of the biochar. This finding agrees favourably with a similar finding reported by Babadi et al. [23] on the sulphonation of beet pulp in the synthesis of acid catalysts. The researchers reported that the total acid density of the biochar increased with an increase in sulphonation time, and an optimum total acid density was obtained after 6 hrs of sulphonation time.

3.4. Optimization of sulphonation process of rubber seed shells biochar

The optimization of the sulphonation process of rubber seed shells biochar based on Equation 3 was performed using the numerical optimization tool of the Design Expert. The sulphonation process variables were constrained to favour the feasibility and economics of the process. Hence, the sulphonation temperature, sulphonation time, and acid-to-biochar ratio were minimized while the response (total acid density of the sulphonated biochar) was maximized. Table 5 shows the numerical optimization solution obtained for the process and the best solution was carefully chosen based on the highest desirability value. The results show that the optimum acid-to-biochar ratio, sulphonation temperature, and sulphonation time were 10:1 (v/w), 98 ^oC, and 4 hrs respectively. The corresponding optimum total acid density was 3.077 mmol/g. The optimum biochar's total acid density of 3.077 mmol/g obtained in this study was slightly lower than the 3.21 mmol/g reported by Endut et al. [19] for sulphonated coconut shell biochar. However, the operating conditions (acid-to-biochar ratio of 12.5:1, sulphonation temperature of 100 ^oC, and sulphonation time of 15 hrs) required to achieve the result were much higher than those of this study.

Table 5: Numerical optimization of rubber seed shells sulphonation process

No.	Acid-to-biochar ratio (v/w)	Sulphonation temp. (^oC)	Sulphonation time (hr)	Total acid density (mmol/g)	Desirability	
1	10.000	98.080	4.000	3.077	0.921	selected

Table 6: Validation of rubber seed shells sulphonation model

No.	Acid-to-biochar ratio (v/w)	Sulphonation temp. (°C)	Sulphonation time (hr)	Predicted total acid density (mmol/g)	Observed total acid density (mmol/g)
1	10:1	98	4	3.077	2.978
2	10:1	98	4	3.077	3.101
3	10:1	98	4	3.077	3.096

The model for rubber seed shells biochar sulphonation was validated by conducting a sulphonation experiment on the biochar under the optimum process conditions obtained in section 3.4. The experiment was replicated three times and the results are shown in Table 6. The experimental optimum average of total acid density of 3.058 ± 0.060 mmol/g is close to the predicted optimum total acid density of 3.077 mmol/g. These results, therefore, validate the robustness of the correlation between the experimental and the predicted total acid density of the sulphonated biochar.

4. Conclusion

The sulphonation of biochar produced from the carbonization of rubber seed shells has been investigated and the process optimized. Acid-to-biochar ratio, sulphonation temperature, and sulphonation time were found to positively influence the attachment of the sulphonic group to the surface of the biochar. The large optimum value of the total acid density (3.06 mmol/g) of the biochar obtained in this study is an indication that the sulphonated biochar is a potential catalyst for the esterification of highly acidic vegetable oil in biodiesel production. This study has established that rubber seed shells, low-grade agricultural wastes, can be utilized in the production of activated carbon with characteristics suitable for catalyzing the esterification of acidic oil. This will enhance the mitigation against environmental pollution resulting from the direct burning of this biomass which is the traditional practice.

Nomenclature

RSS	Rubber seed shells
RSS-BC	Rubber seed shells biochar
CCD	Central composite design
C. V	Correlation variation
ANOVA	Analysis of variance
R^2	Coefficient of determination
Adeq. Prec.	Adequate precision
Adj R^2	Adjusted coefficient of determination
Pred. R^2	Predicted coefficient of determination

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